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Inorganic molecular sieve loaded with dyestuff, process for its preparation and its use as a pigment or material for optical data storage

The invention relates to inorganic molecular sieves loaded with dyestuff having at least one water-insoluble organic dyestuff incorporated irreversibly into the hollow space structure and having a molecular size which corresponds to not more than the size of the hollow spaces of the molecular sieve and is greater than the free pore diameter thereof, and to a process for their preparation.

These molecular sieves can be employed both as pigments in paints and plastics and as optical data storage substances for WORM and EDRAW memories.

The invention relates to an inorganic molecular sieve loaded with dyestuff, a process for its preparation and its use as a pigment or material for optical data storage.

Molecular sieves which comprise metal salts as coloring components have been known for a long time under the name "ultramarine dyestuffs" (German Reichspatent No. 1. 1877). They are prepared, for example, by heating zeolite molecular sieves with alkali metal sulfides at temperatures above 300°C in a nonoxidizing atmosphere and subsequently in an oxidizing atmosphere (see, for example, JP-A-54-142 238 and JP-A-55-071 762).

Organic dyestuffs are as a rule applied to the molecular sieve by treating colorless molecular sieves with dyestuff solutions (see, for example, JP-A-63-017 217; JP-A-53-022 094 and JP-A-75-008 462). There is the risk here, especially in the case of neutral dyestuffs which are adsorbed little on the molecular sieve matrix, that these can be washed off again from the molecular sieve on addition of solvents.

For the preparation of specific zeolite or silicon molecular sieves in particular, processes are also known in which water-soluble basic organic dyestuffs are added to the reaction solution as synthesis-controlling additives (US Patent 40 18 870; GB Patent 14 53 115; US Patent 45 82 693). Since as a rule very bulky triphenylmethane dyestuffs which suppress the formation of undesirable zeolites or silicon molecular sieves by surface adsorption and thus render the

synthesis of specific zeolites or silicon molecular sieves possible are employed, no incorporation into the hollow space structure of the resulting molecular sieves is to be observed.

Another possibility for synthesis of specific zeolite or silicon molecular sieves is the use of templates which are dissolved in the aqueous reaction solution. Templates which are used are as a rule quaternary ammonium salts (European Patent 0 231 018) which function as centers for the hollow spaces to be formed. However, US Patent 4 018 870 also describes the use of methylene blue and acriflavin, both water-soluble basic organic dyestuffs, as templates. To obtain molecular sieves with free pores and hollow spaces, the organic template compounds included in the hollow spaces of the resulting molecular sieves are burned off.

Zeolites and zeolite-like materials in particular are now no longer used only as molecular sieves, but are widely used, for example, in heterogeneous catalysis. Non-dyed zeolites are used alongside TiO_2 as fillers in papermaking (EP-A-0 257 304) or as extenders for emulsion paints (US Patent 4 510 254; JP-A-59-133 265).

Colorings adsorbed onto inorganic carriers can be used as pigments which can be employed in coatings and emulsion paints (Japanese Patent 75-008 462). These pigments are often zeolites and zeolite-like materials loaded with basic dyestuffs.

When using these pigments, it is necessary to choose the composition of the paint such that the colored

pigment is insoluble in the solvent used, sediments uniformly, which is of importance for mixed paints in particular, and does not react with the surrounding medium.

As a result, many solvents which are of interest for paint preparation are excluded, and the possibilities of preparation of mixed paints using the pigments described are severely limited.

Organic dyestuffs can also be used for optical data storage. A distinction is made here between irreversible data storage (WORM = Write Once Read Many) and reversible data storage (EDRAW = Erasable Direct Read After Write). While optical data memories of the WORM type are already known, it has so far been possible to test reversible optical data memories (photochromic systems) only with an inadequate cycle number (10^2 to 10^3 less than in the case of magnetic storage media). The use of "Spectral Hole Burning" at 4K has so far also not led to noticeable improvements in the field of optical EDRAW memories (H. Dürr, Angew. Chem. 101,427 (1989)).

The dyestuffs suitable for irreversible data storage (WORM) can be destroyed by irradiation with light of suitable wavelength and energy. This leads to the formation of holes, bubbles, pits or photochromic changes in color in the carrier material, which result in a change in the reflection properties and therefore in detectability of these points (see M. Emmelius et al., Materialien für die optische Datenspeicherung, [Materials for optical data storage], Angewandte Chemie, 101, 1475

(1989)). In these optical data memories of the WORM type containing dyestuff, polymers are used as a host for the dyestuff molecules.

Since data memories of the WORM type are employed most suitably for archiving data, these memories should have a long life and a high reliability of data reproduction. The following requirements are therefore imposed on optical data memories of the WORM type containing dyestuff:

- Stability to light.
- Stability to "fraying" of the information spot.
- Stability to photocorrosion.

The causes of a lack of stability are local overheating, free radical reactions and reactions of the dyestuff with the carrier material.

The following requirements are imposed on reversible optical data memories (EDRAW type) containing dyestuff:

- Stability to light.
- High cycle number in switch molecules.
- Stability to bleaching, "fraying" of the information spot, photocorrosion.
- Conformation stability.

Here also, the causes of a lack of stability for the EDRAW memories tested in research are local overheating and free radical reactions, as well as reactions of excited dyestuff molecules with other dyestuff molecules in the base state or with the polymer matrix, which leads to irreversible changes to the

dyestuff.

The following requirements are therefore imposed on the host for the dyestuff molecules in the EDRAW memories containing dyestuff:

- high heat distortion point,
- very high dimensional stability during preparation,
- mechanical rigidity,
- no swelling and shrinkage,
- transmission in the visible, ultraviolet and near infrared range (NIR range: 700 - 1100 nm),
- purity and optical homogeneity.

It has not yet been possible to provide any materials which fulfill these criteria satisfactorily.

The object of the present invention is to provide a material which comprises organic dyestuffs in firmly bonded form, meets the requirements for colored pigments or materials for optical data storage and does not have the disadvantages mentioned.

This object is achieved according to the invention by an inorganic molecular sieve loaded with dyestuff, which is characterized in that at least one water-insoluble organic dyestuff having a molecular size which corresponds to not more than the size of the hollow spaces of the molecular sieve and is greater than the free pore diameter thereof is incorporated irreversibly into the hollow space structure of the molecular sieve.

Among the inorganic molecular sieves, zeolites are preferred. The preferred zeolites include, for example, zeolite X, zeolite Y, zeolite L, mordenite, ZSM

5, ZSM 11, offretite, zeolite omega, zeolite β , 25M 34, 25M 39 and FU 1. Zeolites of the faujasite type, such as zeolite X and zeolite Y, are particularly preferred.

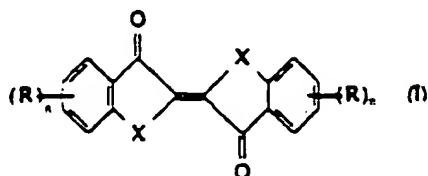
Other suitable inorganic molecular sieves are, for example, silicalites, such as silicalite 1 and silicalite 2, alumophosphates (AlPO), such as AlPO_{4-5} , AlPO_{4-11} and AlPO_{4-14} , and silicon aluminium phosphates (SAPO), such as SAPO 5, SAPO 11, SAPO 31, SAPO 34, SAPO 36, SAPO 37, SAPO 41 and SAPO 46, as well as metal-modified forms of the molecular sieves mentioned; the modifying metals are, for example, Mg, Fe, Co, Zn, Mn, Be, Ti and Ga.

Molecular sieves, in particular zeolites and zeolite-like materials, are determined by a system of hollow spaces. The accesses to these hollow spaces, which are called windows or pore openings, form a three-dimensional sieve, the mesh widths of which depend on the chemical composition and the structure type of the molecular sieves. The mesh width or pore size is, for example, 0.3 - 0.5 nm for zeolite A and 0.7 - 0.8 nm for zeolite X and Y. Data on the structure and hollow space and pore size of inorganic molecular sieves, in particular of zeolites and zeolite-like materials, are summarized in the following publications: D.W. Breck, "Zeolite Molecular Sieves: Structure, Chemistry and Use", John Wiley & Sons 1974; A. Dyer, "An Introduction to Zeolite Molecular Sieves", John Wiley & Sons, 1988.

Examples of the water-insoluble organic dyestuffs which can be incorporated irreversibly into the inorganic

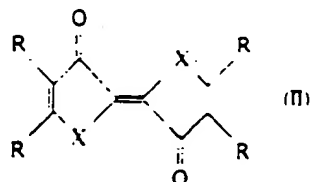
molecular sieve according to the invention are given below:

- indigo and indigoid dyestuffs of the general formula (I)



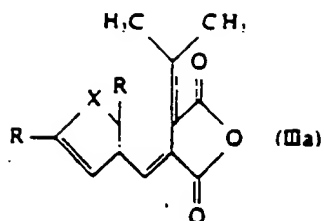
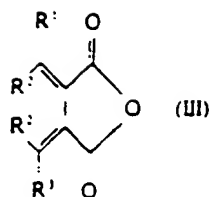
wherein x is NR, S, Se or O, n is an integer from 1 to 4 and the radicals R, which can be identical or different, are hydrogen, substituted or unsubstituted alkyl having 1 - 4 C atoms, substituted or unsubstituted aryl having 6 - 10 C atoms, halogen, amine, monoalkylamine, dialkylamine, alkoxyl and thioalkyl;

- tetra-substituted pyrrolindigo of the general formula (II)



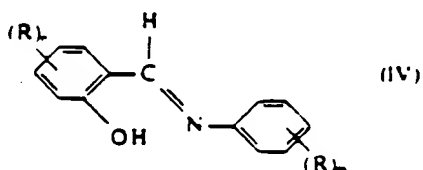
which can be in the cis or trans configuration and wherein X and R are defined as in formula (I) or the radicals R can be bonded to one another to form a substituted or unsubstituted alkyl ring or to form a substituted aliphatic or aromatic heterocyclic radical;

- fulgides of the general formula (III) or (IIIa)



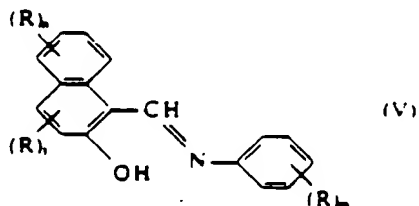
wherein R^1 and R^3 are identical or different and are hydrogen or methyl, R^2 is methyl or unsubstituted or substituted phenyl, the radicals R can be identical or different and are methyl or unsubstituted or substituted phenyl and X is O or S.

- anils of silicyaldehydes of the general formula (IV)



wherein n and R are defined as in formula (I) and m is an integer from 1 to 5;

- anils of o-hydroxynaphthaldehydes of the general formula (V)



wherein R and n are defined as in formula (I), m is an

integer from 1 to 5 and l is 1 or 2.

A molecular size which corresponds to the hollow spaces of the preferred zeolites X and Y but which is above the free pore diameter thereof is shown, for example, by the dyestuffs to be assigned to the general formula (I)

indigo, thioindigo, 5,5'-dichloro-7,7'-dimethylthioindigo, 5,5'-dichloro-4,4',7,7'-tetramethylthioindigo, 5,5'-dichloro-4,4'-dimethylthioindigo, 6,6'-diethoxythioindigo, 5,5'-7,7'-tetramethylthioindigo, perinaphthothioindigo (10), Vat Scarlet G (16), selenium-indigo, oxindigo, di-(N-methyl)indigo, di-(N-ethyl)indigo and di-(N-methyl)-5,5',7,7'-tetrabromoindigo,

the dyestuffs to be assigned to the general formula (II) tetramethylpyrroleindigo, tetramethylpyrrolethioindigo and Helidon Scarlet S,

the dyestuffs to be assigned to the general formula (IIIa)

Aberochrom 540, Aberochrom 999, α,σ -diphenylfulgide, α - p -nitrophenyl- σ -phenylfulgide, α -3,5-dimethoxyphenyl- σ,σ -dimethylfulgide and α -3,4,5-trimethoxyphenyl- σ,σ -dimethylfulgide,

the dyestuffs to be assigned to the general formula (IV) N- p -methylsalicylideneaniline, N-salicylidene- p -anisdine, N-salicylidene- m -toluidine, N-salicylidene-(o -chloro)aniline, N,N'-disalicylidene- m -phenylenediamine, N,N'-disalicylidene- p -phenylenediamine, N-salicylidene-(p -bromo)aniline, N-salicylidene-(p -chloro)anilin and N-salicylidene-(p -nitro)aniline,

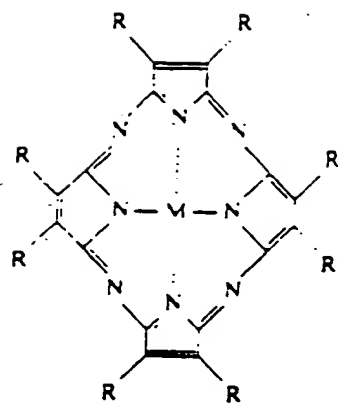
and the dyestuffs to be assigned to the general formula (V)

N-(2-hydroxy)-1-naphthylideneaniline, ethyl N-(2-hydroxy)-1-naphthylidene-p-aminobenzoate, N-(2-hydroxy)-1-naphthylidene-p-anisidine, N-(1-hydroxy)-2-naphthylidene-p-anisidine, ethyl-N-(1-hydroxy)-2-naphthylidene-p-aminobenzoate and N-(1-hydroxy)-1-naphthylidene-(p-bromo)aniline.

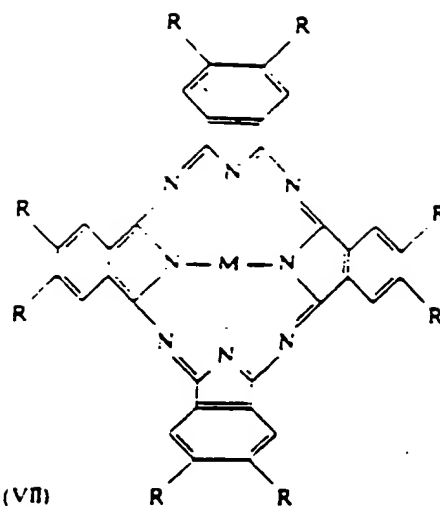
Indigo and thioindigo are preferred.

Seleniumindigo, oxindigo, thioindigo and derivatives thereof and the dyestuffs of the general formulae (III), (IV) and (V) can be changed reversibly by the action of light of a certain wavelength such that their light absorption properties change. These reactions are described below.

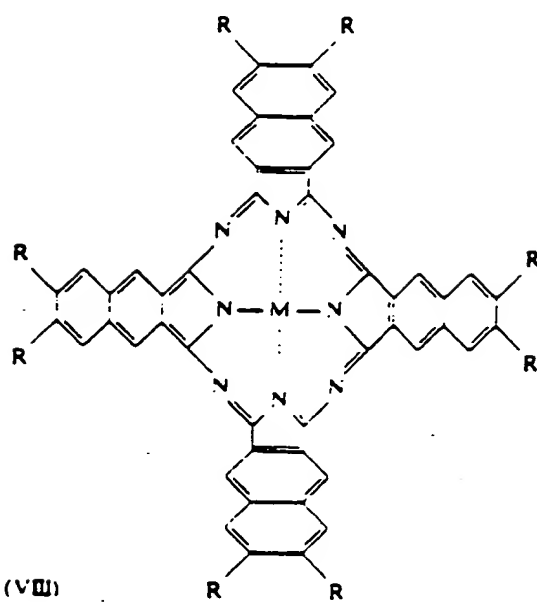
Further examples of water-insoluble organic dyestuffs which are used according to the invention and can be incorporated irreversibly into an inorganic molecular sieve are tetraazo porphyrins of the general formula (VI), phthalocyanines of the general formula (VII), naphthalocyanines of the general formula (VIII), porphyrins of the general formula (IX) and tetrabenzoporphyrins of the general formula (X):



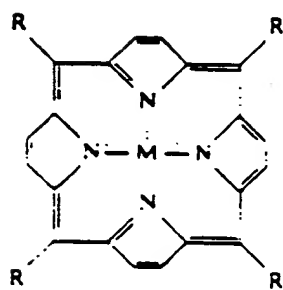
(VI)



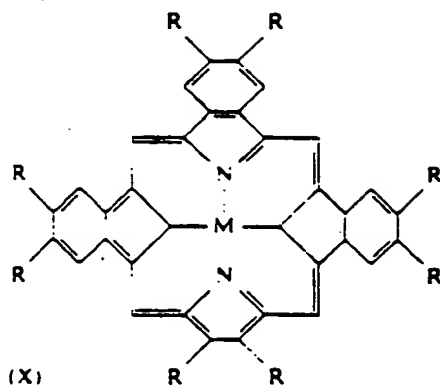
(VII)



(VIII)



(IX)



(X)

wherein M is, for example, 2 hydrogen atoms, Zn(II),

Co(II), Fe(II) or Al(III) and R is hydrogen, branched or unbranched alkyl groups, preferably having 1 - 6 C atoms, substituted or unsubstituted aryl groups, preferably having 6 - 10 C atoms, or groups which contain heteroatoms, such as O or S in ether or thioether groups.

The dyestuffs of the general formulae (VI) to (X) preferably have absorption maxima in the near infrared range (NIR) and can be changed irreversibly by the action of light of certain wavelengths. Preferred dyestuffs of the general formulae (VI) to (X) are metal complexes of 2,3,7,8,12,13,17,18-octahexylthiotetraazoporphyrin;

2,9,16,23-tetrahexylphthalocyanine,

tetrasulphthalocyanine,

2,9,16,23-tetra-(4-(N-methylpyridinium)oxy)phthalocyanine,

2,3,9,10,16,17,23,24-octabutoxyphthalocyanine,

tetra-2,3-(4-(N-methylpyridino))porphyrine;

5,10,15,20-tetraphenylporphyrin,

5,10,15,20-tetrasulphporphyrin,

5,10,15,20-tetra-(4-N-methylpyridinium)porphyrin;

2,11,20,29-tetra(4-methylpyridinium)naphthalocyanine,

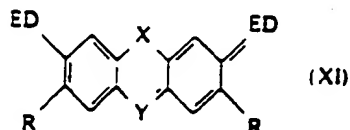
2,11,20,29-tetra-tert-butyl-naphthalocyanine and

2,9,16,23-tetra-tert-butyl-tetrabenzoporphyrin.

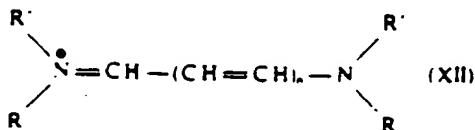
If the inorganic molecular sieves according to the invention laden with dyestuff are used, in particular, as optical data memories, it is expedient for water-soluble organic dyestuffs also to be incorporated into the molecular sieve in addition to the water-

insoluble organic dyestuffs, the molecular size of these water-soluble organic dyestuffs corresponding to not more than the free pore diameter of the molecular sieve. The water-soluble organic dyestuffs are preferably incorporated irreversibly into the molecular sieve.

Water-soluble cationic organic dyestuffs from the group comprising arylmethine dyestuffs and aza analogs thereof, cyanine dyestuffs and cationic azo dyestuffs which correspond to the general formulae (XI) to (XIV), are preferably incorporated into molecular sieves having an anionic lattice, such as zeolites:

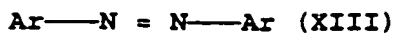


wherein X is CH, CR, S, O, N, NR or NH; Y is O, H, NR⁺, NH⁺, CR or CH; the group =ED is an electron donor, such as =NR₂, =NRH⁺, =NH₂ or =O; and the radicals R can be identical or different and are hydrogen, a branched or unbranched alkyl group having 1 to 6 C atoms or a substituted or unsubstituted aryl group having up to 6 C atoms, with the proviso that the groups Y, R and ED are chosen such that the resulting dyestuff molecule is cationic;

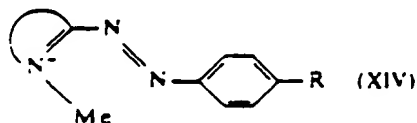


wherein n is not more than 2, R and R' can be identical or different and are hydrogen, a substituted or unsubstituted alkyl group having 1 - 6 C atoms or a substituted

or unsubstituted aryl group having up to 10 C atoms, or wherein R and R' can be bonded to one another and, with the N atom, form a heterocyclic radical;

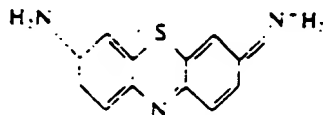


wherein the groups Ar are substituted or unsubstituted phenyl, pyridyl or naphthyl groups, which can be identical or different, and the substituents are chosen from the group comprising H, -OR, -NO₂, -halogen, -alkyl, -NR₃ and -NR₂ such that the resulting dyestuff molecule is cationic, and wherein R is hydrogen or an alkyl group having 1 - 6 C atoms;

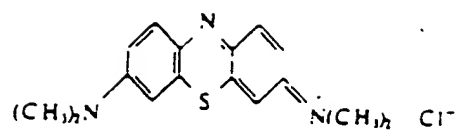


wherein R is a nitro or dimethylamino group and the heterocyclic radical is a substituted or unsubstituted five- or six-membered nitrogen or sulfur heterocyclic radical.

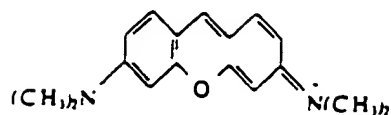
Examples of dyestuffs of the general formulae (XI), (XII) and (XIII) which are suitable according to the invention are the dyestuffs falling under the general formula (XI) azure A, azure B, azure C, mauvein, Basic Blue 4, thionine



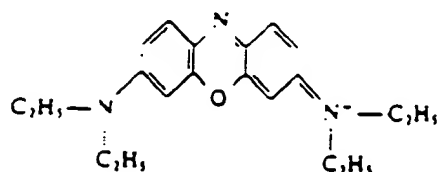
methylene blue



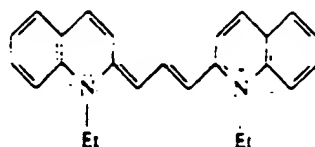
Pyronine G



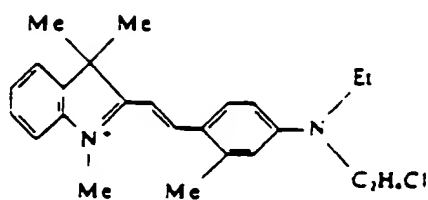
and Basic Blue 3



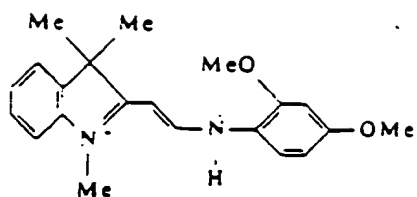
the dyestuffs falling under the general formula (XII)
pinacyanol



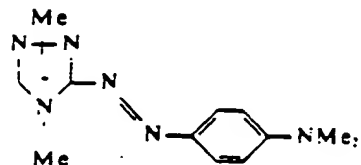
Basic Violet 7



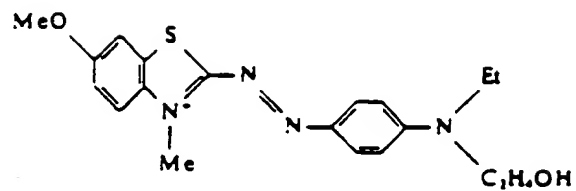
Basic Yellow 11



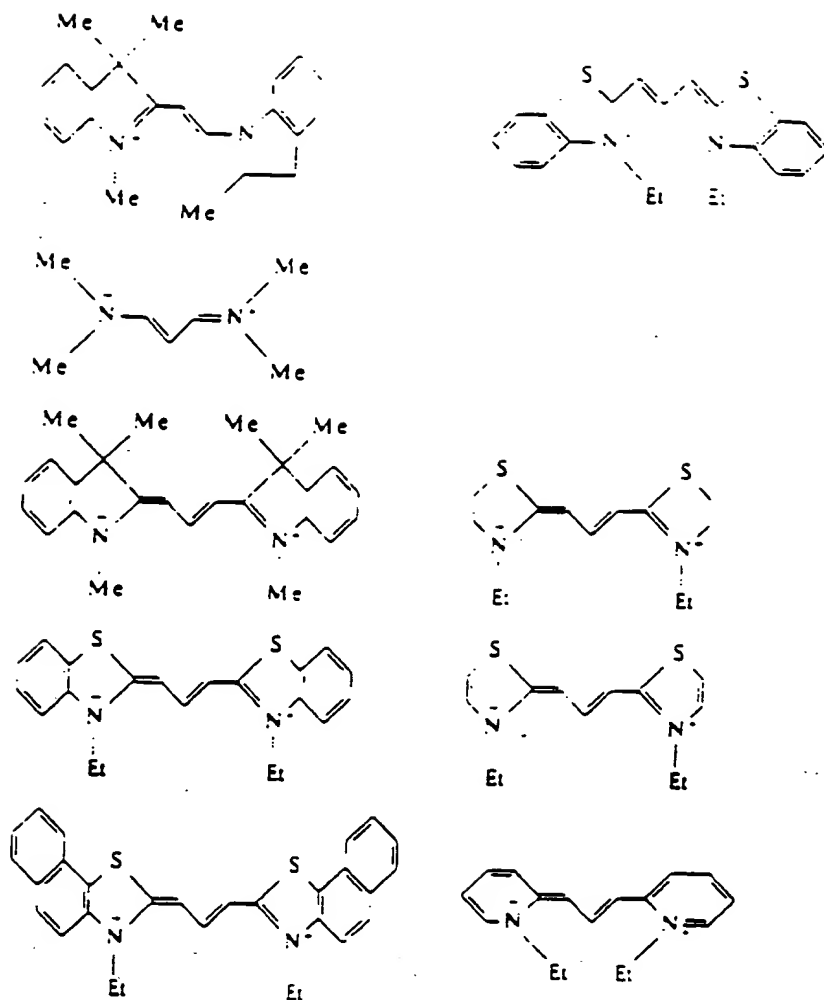
Basic Red 22



Basic Blue 41



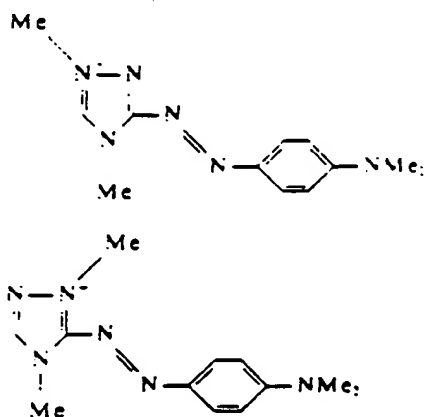
and the dyestuffs having the following structures:



the dyestuffs falling under the general formula (XIII)

2-methoxyazobenzene, 2-hydroxyazobenzene, 3-methylazobenzene, 3-nitroazobenzene, 3-methoxyazobenzene, 3-hydroxyazobenzene, 4-fluoroazobenzene, 4-methylazobenzene, 4-carbomethoxyazobenzene, 4-methoxyazobenzene, 4-dimethylaminoazobenzene, 4-aminoazobenzene, 4-N(CH₃)₃-azobenzene, 4'-phenyl-4-dimethylaminoazobenzene, 4'-hydroxy-4-dimethylaminoazobenzene, 4,4'-bis(dimethylamino)azobenzene, 2-methyl-4-hydroxyazobenzene, 4'-methyl-4-hydroxyazobenzene, 2,6-dimethyl-4-hydroxyazobenzene, 2,2',4',6'-tetramethyl-4-hydroxyazo-

benzene, 2,2',4',6,6-pentamethyl-4-hydroxyazobenzene, 4'-chloro-4-hydroxyazobenzene, 2',4'-dichloro-4-hydroxyazobenzene, 2,2',4',6'-tetrachloro-4-hydroxyazobenzene, 2,2'-dimethoxyazobenzene, 3,3'-dimethylazobenzene, 4,4'-dimethylazobenzene, 4-nitro-4'-methoxyazobenzene, 2-hydroxy-5-methylazobenzene, 1,4-diphenylazobenzene, 4,4'-diphenylazobenzene, 2,2'-azopyridine, 3,3'-azopyridine, 4,4'-azopyridine, 2-phenylazopyridine, 3-phenylazopyridine, 1-phenylazonaphthalene, 1,1'-azonaphthalene, 1,2'-azonaphthalene and 2,2'-azonaphthalene, and the diazahemicyanine dyestuffs falling under the general formula (XIV), in which R is $N(CH_3)_2$ and the heterocyclic radical is tetrazolyl, imidazol-2-yl, 1,2,4-triazol-2-yl, indazol-3-yl, pyridin-2-yl, 5-methyl-1,3,4-thiadiazol-2-yl, quinolin-2-yl, thiazol-2-yl, benzothiazol-2-yl, 3-methyl-isothiazol-5-yl, β -naphthothiazol-2-yl or benzothiazol-3-yl, or in which R is NO_2 and the heterocyclic radical is 6-methoxybenzothiazol-2-yl, and the dyestuffs falling under the general formula (XIV) having the following structures:



From this group of cationic dyestuffs, methylene

blue, thionine and pyronine G are particularly preferred.

Anionic dyestuffs are preferably incorporated into molecular sieves having a cationic lattice, such as SAPO.

The dyestuff loading of the inorganic molecular sieves according to the invention is preferably in the range from 10^{-6} to 10^{-4} mol of dyestuff per g of molecular sieve, and in particular about 10^{-5} mol of dyestuff per g of molecular sieve, based on the total amount of dyestuff.

The inorganic molecular sieves according to the invention loaded with dyestuff can be prepared via template syntheses. Templates, such as organic amines, ammonium compounds, imines and iminium compounds, are substances which act as molecular patterns during synthesis and with the aid of which it is possible to form hollow spaces in molecular dimensions in a solid matrix. Amines, such as triethylamine and triethanolamine, are preferably used in the process according to the invention.

Zeolites and zeolite-like molecular sieves are preferably prepared by template syntheses. An overview of the templates suitable for the synthesis of the individual zeolites or zeolite-like molecular sieves is given in D.W.Breck "Zeolite Molecular Sieves: Structure, Chemistry and Use", John Wiley & Sons (1974).

The principle of template synthesis of molecular sieves is explained in more detail below using the example of a zeolite X.

An aqueous aluminate solution, a soda water glass solution and the template are stirred with one another and, after gel formation has taken place, seed crystals are added. When the crystal growth has ended, the zeolite crystals are filtered off, washed to a neutral pH with water and dried.

If at least one water-insoluble organic dyestuff is dissolved in the template or dissolved in a suitable organic solvent together with the template in the process according to the invention, it is possible for dyestuffs to be incorporated in a controlled manner into the hollow space structure of the inorganic molecular sieves, in particular of the zeolites. When the crystal growth has ended, colored molecular sieves, in particular zeolites, are obtained and are likewise filtered off, washed to a neutral pH with water and dried. These colored molecular sieves are then extracted with a solvent in which the dyestuff employed is readily soluble, in order to remove excess, i.e. non incorporated, dyestuff. Colored zeolites which can no longer release dyestuff in solution are thus obtained with water-insoluble organic dyestuffs.

It is possible for several water-insoluble organic dyestuffs to be dissolved simultaneously in the template or in a suitable organic solvent together with the template and to be incorporated into the inorganic molecular sieve. The total concentration of water-insoluble dyestuff in the template or in the template-containing solution is preferably 10^{-1} to 10^{-6} mol/l.

Suitable organic solvents in which the template

and the dyestuff can be dissolved are, for example, pyridine, glycols, glycerol, DMSO, DMF and N-methylpyrrolidone (NMP). The amount of dyestuff and solvent together is preferably approximately 1 to 10% by weight, based on the template.

The molecular sieves according to the invention loaded with dyestuff, which can be obtained as described above, can be loaded with at least one water-soluble organic dyestuff by treating them with an aqueous solution of at least one water-soluble organic dyestuff, the molecular size of which corresponds to not more than the free pore diameter of the molecular sieve. In order to bond the dyestuffs firmly to the molecular sieve in this case also, molecular sieves with an anionic lattice should preferably be reacted with aqueous solutions of cationic dyestuffs, in particular of the general formulae (XI) to (XIII). Molecular sieves with a cationic lattice are preferably reacted with aqueous solutions of anionic dyestuffs.

By treating molecular sieves with aqueous solutions of water-soluble organic dyestuffs, the molecular size of which corresponds to not more than the pore diameter of the molecular sieve, the dyestuff molecules penetrate into the outer pores of the molecular sieve and are bonded firmly via ionic bonds. The concentration of the aqueous solution of the water-soluble organic dyestuff is preferably at a total concentration of dyestuff of 10^{-1} to 10^{-6} mol/l.

The inorganic molecular sieves obtained by the

process according to the invention, in particular the zeolites, have a uniform crystallinity and roughness and usually have a particle size of 1 - 20 μm . They are used in various industrial fields.

Non-bleeding opaque pigments can be obtained from organic coloring agents by the process according to the invention, it being possible for the color strength to be regulated by the amount of dyestuff supplied. The inorganic molecular sieves according to the invention loaded with dyestuff which can be employed as pigments comprise only a fraction of the dyestuff which would otherwise be required for a pigment.

Because of their different chemical compositions, conventional pigments have very different specific gravities. If these are employed in paints and coatings, partial demixing of the paint may occur, especially in mixed paints and coatings, if the pigments settle to very different degrees. However, paint and coating additives which prevent settling can be used to only a limited extent, since they adversely influence other paint and coating properties.

In the preparation of pigments from different-colored molecular sieves according to the invention loaded with dyestuff, because of the very similar chemical compositions - organic dyestuff, preferably in an aluminosilicate or silicon aluminium phosphate matrix - of the individual molecular sieves, their uniform size and their similar specific gravities, no demixing is found during sedimentation. Encapsulating the dyestuff in

the host lattice increases the stability of the pigments towards other constituents of the paint and prevents bleeding out of the organic dyestuff. Any desired solvents which do not attack the molecular sieve matrix can be employed here in the paints and coatings. In the case of monodisperse distribution of the dyestuff in the host, new materials are provided, the properties of which lie between dissolved and crystalline dyestuffs.

The inorganic molecular sieves according to the invention loaded with dyestuff furthermore are non toxic, since the dyestuffs are bonded firmly in the host lattice. They are therefore outstandingly suitable for replacing heavy metal pigments in paints and coatings.

The inorganic molecular sieves according to the invention loaded with dyestuff can also be employed as pigments in all types of plastics and are a non toxic substitute for heavy metal pigments, without the plastics losing their brilliance of color.

Because of the low amounts of dyestuff they comprise (preferably 10^{-6} to 10^{-4} mol of dyestuff per g of molecular sieve), the molecular sieves according to the invention loaded with dyestuff are very inexpensive to prepare.

Depending on the choice of the organic dyestuff incorporated, the inorganic molecular sieves according to the invention loaded with dyestuff can also be used as materials for optical data storage.

If the dyestuffs incorporated into an inorganic molecular sieve can be denatured by light of a defined

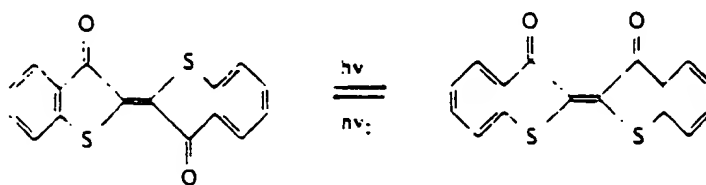
wavelength, the inorganic molecular sieve according to the invention loaded with dyestuff can be used for irreversible data storage (WORM memories). However, practically all the dyestuffs prepared on a large industrial scale having absorptions between 400 and 700 nm are currently of minor interest for optical data storage, since they show no absorption or only slight absorption in the near infrared range (NIR) achieved by cheap diode lasers. The number of NIR dyestuffs has increased sharply in recent years. Among these, complex dyestuffs, such as tetraazoporphyrins, phthalocyanines, naphthalocyanines, porphyrins and tetrabenzoporphyrins of the general formulae (VI) to (X) are preferred.

The advantage of the inorganic molecular sieves according to the invention loaded with dyestuff and employed as WORM memories over conventional WORM dyestuff memories lies in the use of the "spacer effect" of zeolites, by which free radical reactions and other reactions between dyestuff molecules are suppressed, and in the possibility of "multiple loading" of molecular sieves with dyestuffs. By such multiple loading of the molecular sieves with dyestuffs which absorb light of different wavelength, a higher storage density is achieved with the same available space. However, each dyestuff will then also require its own laser for writing or reading.

If photochromic dyestuff systems, such as thio-indigo and/or azobenzenes, are incorporated irreversibly into inorganic molecular sieves, and if a reversible

change in the molecule, such as a change in conformation, cis/trans isomerism, tautomerism or valency isomerism leading to a detectable change in the absorption maximum, is to be observed in these systems when irradiated with light of a suitable wavelength, these materials can be employed for reversible data storage (EDRAW memories). The change described in the dyestuff molecule can be reversed again by light of a different wavelength. The system is accordingly reversible.

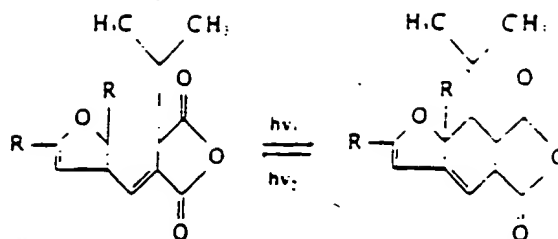
In the case of thioindigo (and thioindigo derivatives), the change in conformation proceeds in accordance with the following equation:



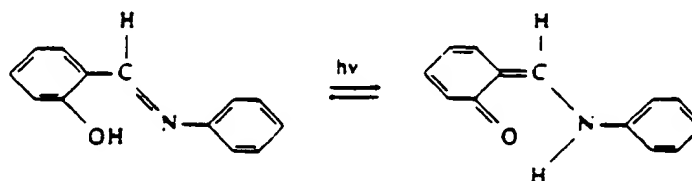
In the case of thioindigo, the absorption maxima shift, for example, from about 545 nm to about 485 nm, which means a shift of about 60 nm. The shift differences are of about the same order of magnitude for thioindigo derivatives. An overview is given in "Color Index" volume 4, page 502/503, 3rd Edition (1975).

In the case of azobenzenes, a rotation about the N=N double bond is observed.

In the case of fulgides of the general formula (III), the following cyclization/ring-opening reaction proceeds reversibly by the action of light of different wavelength:



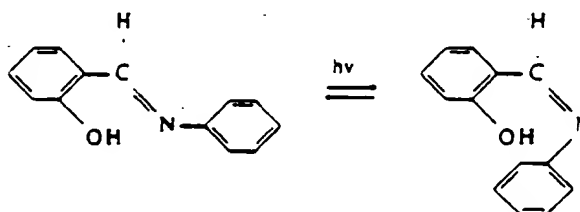
A light-induced tautomerism is observed in the compounds of the general formulae (IV) and (V), shown by way of example with the aid of the tautomeric equilibrium reaction of N-salicylideneaniline:



pale yellow (enol)

red (keto)

However, a photochemical trans/cis isomerism of the enol form can also be observed in these compounds:

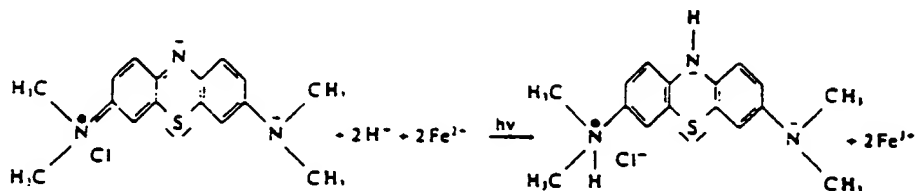


trans-enol

cis-enol

Other methods for reversible data storage in EDRAW memories are "Photochemical and Spectral Hole Burning" (W.E. Moerner, Journal of Molecular Electronics, 1, 55-71 (1985)) or storage via photoredox systems. The inorganic molecular sieves according to the invention loaded with dyestuff can also be used for these possibilities. Methylene blue can be employed, for

example, as a photoredox system. If a molecular sieve loaded with methylene blue is treated with an $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution, the possibility of reversible data storage exists by means of the following reaction



(the leuco form is colorless). A zeolite X or zeolite Y which comprises thioindigo as the water-insoluble dyestuff, is loaded with methylene blue as the cationic dyestuff and has been treated with an $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution is a preferred embodiment of an EDRAW memory.

Another preferred embodiment of the EDRAW memory is an iron-modified zeolite X or Y, which comprises iron ions in the lattice, comprises thioindigo as the water-insoluble dyestuff and is loaded with methylene blue as the cationic dyestuff.

The inorganic molecular sieves according to the invention loaded with dyestuff which are used as materials for optical data storage are preferably embedded in a carrier material. Suitable carrier materials are, for example, the following polymers: polycarbonates, polymethyl methacrylates, polystyrene, polyvinyl chloride, styrene/acrylonitrile copolymers, polyacrylates, polyvinyl alcohols, cellulose acetates and cellulose ethers.

Suitable light sources for optical data storage for WORM and EDRAW memories are, for example, lasers or Xe lamps with an interference filter.

Inorganic molecular sieves, and in particular zeolites, meet all the requirements of the host mentioned at the outset for dyestuff optomemories to a particularly high degree. Inorganic molecular sieves, and in particular zeolites, are chemically inert towards excited free radical dyestuff molecules. The spacer effect due to spacially separate anchoring of individual dyestuff molecules in the cages of the molecular sieve or zeolite hollow space system prevents reciprocal reactive interactions and therefore leads to a higher stability of the optical data memory. Further advantages of these memory materials compared with conventional materials are the following:

- stability and inertness of the carrier;
- good signal/noise ratio in spite of low loading, due to the high molar extension coefficients of the dyestuffs
- low light intensities for the writing and reading operation due to the high molar extension coefficients of the dyestuffs (only lasers of relatively low energy which are available inexpensively and with which local overheating, which reduces the life of conventional memories, is avoided are accordingly required. The energies for lasers employed in connection with the molecular sieves according to the invention loaded with dyestuff are 1 to 50 mW. In conventional systems, on the other hand, lasers having an average energy of about 100 mW are employed for

writing operations);

- multiplication of the memory capacity by multiple loading of the material with dyestuffs of different absorption maxima with the same space requirement (preferably 1 to 10 μm);
- simultaneous reading and writing at different wavelengths, i.e. lowering of the access time and increase of the data transfer rate by multiple loading of the material with dyestuffs of different absorption maxima with the same space requirement (preferably 1 to 10 μm).

The following examples illustrate the invention.

Example 1

Solution A:

To prepare a zeolite NaX with a ratio of Si/Al = 1.1, 13.65 g of $\text{Al}(\text{OH})_3$ and 10 g of NaOH are dissolved in 100 ml of water.

This batch (solution A) is divided up and employed in the reactions in Example 2 and 3 for synthesis of colored zeolites.

Solution B

32 g of soda water glass (DAB6, Merck) are diluted with 600 ml of water, while stirring.

This batch (solution B) is divided up and employed in the reactions in Example 2 and 3 for synthesis of colored zeolites.

Example 2

To prepare a 10^{-3} molar solution, 0.0148 g of

thioindigo is dissolved in 50 ml of TEA (triethanol-amine). This solution is stirred into 300 ml of solution B and the mixture is homogenized at 25°C. 50 ml of solution A are then added, while stirring vigorously. After a gel has formed (after about 10 to 30 minutes), 0.5 g of seed crystals (zeolite NaX, Union Carbide) is stirred in. If delayed gel formation occurs, the seed crystals are added after 40 to 60 minutes. The batch is left to stand in a polyethylene bottle for 2 to 4 weeks at 80°C for crystallization. The formation of crystals has ended when the solid phase formed does not settle further.

The colored zeolite formed is filtered off, washed to a neutral pH with water and dried. The colored zeolite is then extracted with ethanol in a Soxhlet apparatus until (2 to 48 hours) the supernatant solution is colorless and consequently no further physisorbed dyestuff is present on the surface. The resulting red-colored zeolite (NaX) is dried and can then be watered down to the desired extent via a saturated KCl solution.

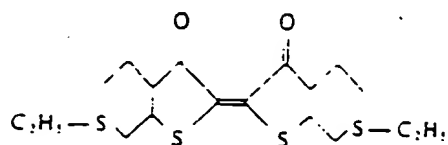
The resulting material is finely crystalline with a particle size of 1 - 20 μm .

Example 3

The reaction is carried out as described in Example 2, but with the difference that for the preparation of a 10^{-3} molar solution 0.020 g of Helidon Scarlet S is dissolved in 50 ml of TEA.

A zeolite NaX colored yellow-orange is obtained as a finely crystalline material as the product, Helidon

Scarlet S:



Example 4

The reaction is carried out as described in Example 2, but with the difference that in addition to the thioindigo, methylene blue is dissolved in the reaction solution and is also incorporated into the zeolite X.

The concentration of methylene blue in solution is varied as shown in Table 1.

Table 1

Concentration of methylene blue [mol/l]	Color achieved
10^{-2}	deep blue
10^{-3}	dark blue
10^{-4}	blue-violet
10^{-5}	pale blue-violet
10^{-6}	pale blue with a reddish tinge

Example 5

The reaction is carried out as described in Example 2, but with the difference that 0.31 mg (10^{-6}

mol) of H_2 -phthalocyanine is dissolved in 50 ml of TEA.

Methylene chloride is used as the extraction solvent.

A zeolite with a weak colored shimmer is obtained as the product. The absorption maxima of the dyestuff incorporated are at about 746, 773 and 835 nm.

Examples 6 and 7

The reaction is carried out as described in Example 5, but with the difference that $Fe(II)$ -phthalocyanine or $Co(II)$ phthalocyanine is dissolved in pyridine in a concentration of 10^{-5} mol/l and 1 % by weight of this solution (based on the TEA) is admixed to the TEA.

One absorption maximum of the iron-containing dyestuff incorporated is at about 774 nm, and one absorption maximum of the cobalt-containing dyestuff incorporated is at about 782 nm.

Example 8

2 g of the zeolite from Example 2 colored with thioindigo and 25 ml of a 10^{-3} molar aqueous solution of methylene blue are shaken constantly at 25°C for 2 days. The colored zeolite is filtered off, washed with water and dried. The colored zeolite is then extracted with ethanol in a Soxhlet apparatus until (2 - 48 hours) the supernatant solution is colorless and consequently no further physisorbed dyestuff is present on the surface. The resulting material is dried and can then be watered down to the desired extent via an aqueous KCl solution.

Example 9

0.5 g of zeolite is shaken with 45 ml of a 0.15 molar FeSO_4 solution, while flushing with nitrogen, for about 1 hour. During this procedure, nitrogen is constantly passed into the suspension. The zeolite is then washed with oxygen-free, freshly distilled water and dried.

The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be influenced by varying the oxygen supply.

CLAIMS

1. Inorganic molecular sieve loaded with dyestuff, characterized in that at least one water-insoluble organic dyestuff having a molecular size which corresponds to not more than the size of the hollow spaces of the molecular sieve and is greater than the free pore diameter thereof is incorporated irreversibly into the hollow space structure of the molecular sieve.
2. Molecular sieve according to claim 1, characterized in that the molecular sieve is chosen from zeolites and zeolite-like materials.
3. Molecular sieve according to claim 1 or 2, characterized in that the water-insoluble organic dyestuff is chosen from the group comprising indigo, indigoid dyestuffs, fulgides, azo dyestuffs and anils of salicylaldehydes and o-hydroxynaphthaldehydes.
4. Molecular sieve according to claim 1 or 2, characterized in that the water-insoluble organic dyestuff can be changed irreversibly by the action of light and is at least one dyestuff from the group comprising tetraazoporphyrins, phthalocyanines, naphthalocyanines, porphyrins and tetrabenzoporphyrins, which can also be present as a metal complex.
5. Molecular sieve according to one of claims 1 to 4, characterized in that at least one water-soluble organic dyestuff, the molecular size of which corresponds to not more than the free pore diameter of the molecular sieve, is additionally incorporated into the hollow space structure of the molecular sieve.

6. Molecular sieve according to claim 5, characterized in that the water-soluble organic dyestuff is a cationic dyestuff from the group comprising arylmethine dyestuffs and aza analogs thereof, cyanine dyestuffs and cationic azo dyestuffs.
7. Molecular sieve according to one of claims 1 to 6, characterized in that the total content of organic dyestuff is in the range from 10^{-6} to 10^{-4} mol of dyestuff per g of molecular sieve.
8. Molecular sieve according to one of claims 1 - 7, characterized in that the molecular sieve loaded with dyestuff is embedded in a carrier material.
9. Process for the preparation of an inorganic molecular sieve loaded with dyestuff according to one of claims 1 to 8 in a template synthesis, characterized in that at least one water-insoluble organic dyestuff, the molecular size of which corresponds to not more than the size of the hollow spaces of the molecular sieve to be synthesized and is greater than the free pore diameter thereof, and which is present dissolved in a suitable organic solvent in a template or together with a template, is incorporated into the molecular sieve during template synthesis thereof, and, if appropriate, the resulting colored molecular sieve is then treated with an aqueous solution of at least one water-soluble organic dyestuff, the molecular size of which corresponds to not more than the free pore diameter of the molecular sieve.
10. Process according to claim 9, characterized in that the template is chosen from the group comprising

organic amines, ammonium compounds, imines and iminium compounds.

11. Process according to claim 9 or 10, characterized in that the water-insoluble dyestuff is employed in a concentration of 10^{-1} to 10^{-6} mol per l of template.
12. Process according to one of claims 9 to 11, characterized in that the aqueous solution of the water-soluble dyestuff has a concentration of 10^{-1} to 10^{-6} mol/l.
13. Use of the inorganic molecular sieve loaded with dyestuff according to one of claims 1 to 8 as a pigment.
14. Use according to claim 13, characterized in that the pigment is employed in paints, coatings and plastics.
15. Use of the inorganic molecular sieve loaded with dyestuff according to one of claims 1 to 8 as a material for optical data storage.
16. Use according to claim 15, characterized in that the data storage material is of the WORM type.
17. Use according to claim 15, characterized in that the data storage material is of the EDRAW type.